POLYCHLOROBIPHENILS (PCBs) IN THE SEDIMENT AND SURFACE WATER OF THE VENICE LAGOON

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INTRODUCTION

Polychlorinated biphenils (PCBs) are ubiquitous environmental contaminants, characterized by their persistence in the environment. Due to their hydrophobic nature, they accumulate in sediments and biota in the acquatic environment.
The Venice Lagoon extends for about 549 Km^2, along the northwest coast of the Adriatic Sea. It is a shallow basin, connected to the sea through three entrances, 400-900 m wide. About 3.1 - 4.5 x 10^8 m^3 of water is exchanged between the lagoon and the sea during a tidal cycle, but only the water in areas near the entrances is significantly exchanged with the sea water. The Venice Lagoon is located in a highly populated area and is subjected to pollution from industrial, agricultural and urban sources. The contamination level varies from area to area of the lagoon and it is indicative of the pollution sources.
In this paper we present analytical procedures for the determination of PCBs in sediment and in surface water ("dissolved" and "particulate") and some data of the PCB concentration determined in samples from the Venice Lagoon.

MATERIALS AND METHODS

Sediment samples were collected at five sites in the Venice Lagoon, selected on the basis of a supposed diversity of input and pollution level. Site 1 (named "Marghera") is located in front of Porto Marghera and its industrial area, where pollution is influenced by industrial inputs; site 2 (named "Dese") is located near the mouth of the Dese river and pollution is influenced by agricultural inputs; site 3 (named "Venice") is located in the urban zone (Grand Canal); site 4 (named "Sessola") is located near the Island of Sacca Sessola and is representative of the central area of the Lagoon; site 5 (named "Chioggia") is located centrally in the southern basin of the Lagoon, an area that is considered as the cleaner part of the Lagoon.
The 0-20 cm layer of sediment sampled was immediately homogenized, sieved, dried at 40 °C for 24 h and stored at 4 °C until analysis. The dried sediment sample (3 g) was extracted in a sonication bath for 2 h using only one aliquot of 50 ml of a mixture of pesticide grade n-hexane-dichloromethane (4:1, v/v). The sample extract was dried by anhydrous Na_2SO_4 and, after sulphur removal by treatment with mercury, was cleaned on a column slurry packed with Florisil and Alumina[1]. The PCBs were eluate with n-hexane collecting 30 ml. The hexane eluate was reduced

under a gentle stream of nitrogen to 100-500 μl and analyzed by gaschromatography-mass spectrometry (GCMS). Prior to extraction, five PCBs which are not significantly present were added to the the sediment samples for use as internal standards in the quantification: PCB30 for the trichlorobiphenyl homolog; PCB77 for the tetrachlorobiphenyl homolog; PCB96 for the pentachlorobiphenyl homolog; PCB166 for the hexachlorobiphenyl homolog; PCB189 for the heptachlorobiphenyl and octachlorobiphenyl homolog.

Water samples were collected at a site located near our laboratory on a wide canal (Canale della Scomenzera) with an average depth of 2.2 m; this canal exchanges water with an area of the Lagoon that exchanges water directly with Adriatic Sea. The water sample was filtered by GF/F Whatman glass filters (0.7 μm). The filtered water was used for the determination of "dissolved" PCBs and the filters with the filtered matter for the determination of the "particulate" PCBs.

In the filtered water "dissolved" PCBs were determined by continuous liquid-liquid extraction[2]. A 10 l volume of Lagoon water was extracted for 24 h using 200 ml of a mixture of pentane-methylene chloride, 2+1 v/v. The water sample extract was dried by anhydrous Na_2SO_4 and reduced to 3 ml under a gentle stream of nitrogen. This solution was cleaned on a column like that used for sediment analysis. The hexane eluate was reduced under a gentle stream of nitrogen to 100 μl and analyzed by GCMS.

For the determination of "particulate" PCBs the filters and the filtered matter corresponding to 10 l of Lagoon water were extracted in a sonication bath for 2 h using only one aliquot of 60 ml of a mixture of pentane-methylene chloride, 2+1 v/v. The extract solution, cleaned in the same way as the extract solution obtained from the water, is reduced under a gentle stream of nitrogen to 100 μl and analyzed by GCMS.

Prior to extraction of water and of particulate five carbon-13-labeled PCBs were added to the sediment samples for use as internal standards in the quantification: PCB28 for the trichlorobiphenyl homolog; PCB52 for the tetrachlorobiphenyl homolog; PCB118 for the pentachlorobiphenyl homolog; PCB153 for the hexachlorobiphenyl homolog; PCB180 for the heptachlorobiphenyl homolog.

Data were acquired in the electron impact (EI) mode (70 eV) using the selected ion monitoring (SIM) technique; the ion masses used in the acquisition were: 256 for TriCBs; 292 for TetraCBs; 326 for PentaCBs; 360 for HexaCBs; 394 for HeptaCBs; 430 for OctaCBs; 464 for NonaCBs.

PCB quantification was made by direct comparison of the PCB peak area in the chromatogram with that of the PCB used as the reference standard.

Results and Discussion

Average values of the PCB concentration found in the sediments of the five areas considered are reported in Tab. 1. The values of the areas named "Marghera", "Dese", "Venice" and "Chioggia" are the average of three independent samples, while that of the area named "Sessola" is the average of two independent samples. It is surprising to observe that the samples with the greater concentration of PCBs come not from the industrial area ("Marghera"), but from the urban area ("Venice"). In this area the PCB concentration is on average 5-10 times greater than that found in other areas. Different behaviour is shown by the congeners of the trichlorobiphenyl homolog, which show a similar concentration level. The concentration values in the areas show high

Tab.1. Average values of the PCB concentration (ng/g) found in the sediment samples of five sites of the Venice Lagoon.

PCB No.	Sites				
	Marghera	Dese	Venice	Sessola	Chioggia

15,18	1.147	1.578	1.042	0.887	1.519
31,28	1.711	1.979	2.769	1.117	1.784
20,33	0.476	0.549	0.803	0.305	0.508
52	0.554	0.540	3.117	0.327	0.306
49	0.221	0.218	1.121	0.130	0.120
44	0.233	0.308	1.112	0.127	0.154
74	0.230	0.190	0.928	0.140	0.110
70	0.310	0.284	1.778	0.194	0.166
66	0.462	0.354	1.719	0.318	0.226
60,56	0.248	0.246	0.866	0.141	0.158
95	0.435	0.551	3.806	0.329	0.222
91	0.137	0.135	1.045	0.088	0.045
90,101	0.887	0.796	7.110	0.635	0.317
99	0.588	0.455	4.439	0.517	0.182
97	0.180	0.207	1.677	0.131	0.060
87,115	0.235	0.318	2.263	0.133	0.083
85	0.129	0.125	0.975	0.083	0.035
110	0.792	0.801	6.872	0.528	0.247
123	0.135	0.090	0.985	0.094	0.047
118	0.927	0.743	7.673	0.742	0.281
105	0.336	0.331	2.758	0.230	0.100
151	0.210	0.120	0.860	0.097	0.094
135	0.158	0.073	0.641	0.058	0.053
149	1.083	0.611	4.995	0.461	0.398
146	0.272	0.119	0.980	0.130	0.091
132,153	1.904	0.943	8.636	0.898	0.684
141	0.170	0.089	0.870	0.059	0.075
176	0.659	0.294	3.112	0.292	0.210
138,158	1.144	0.610	5.707	0.535	0.377
128	0.193	0.129	1.165	0.112	0.069
156	0.149	0.103	1.046	0.084	0.064
179	0.166	0.063	0.452	0.050	0.061
187	0.672	0.183	1.473	0.213	0.175
183	0.231	0.091	0.745	0.069	0.076
180	1.096	0.339	3.291	0.331	0.335
170,190	0.379	0.144	1.432	0.129	0.148
199	0.286	0.041	0.350	0.053	0.055
203,196	0.283	0.048	0.422	0.068	0.057
194	0.512	0.079	1.276	0.103	0.099
Sum	19.939	18.877	92.314	10.938	9.782

Tab. 2. “Dissoled” and “particulate” concentration of PCBs (pg/l) found in a sample of water of the Canale della Scomenzera.

PCB No.	“dissolved”	“particulate”	PCB No.	“dissolved”	“particulate
15,18	50	5	110	96	64

31,28	91	21	82,151	21	25
52	139	31	135	10	14
49	52	13	149	46	59
47,48	29	8	118	68	69
44	56	15	146	10	16
41,64	29	7	132,153	82	137
74	23	8	105	18	21
70	50	21	141	14	24
95	104	48	138,158	50	111
91	15	7	187	17	34
90,101	110	75	183	8	18
99	46	31	128	8	17
97	27	18	174	15	33
87,115	55	39	180	28	89
85	20	13	170,190	12	50
136	13	13	Sum	1437	1153

correlation coefficients, mostly $0.950<r<0.999$, for all the PCB congeners (e.g., $r_{PCB52\text{-}PCB110}= 0.998$; $r_{PCB99\text{-}PCB141}= 0.994$) indicating a uniformly distributed kind of pollution, that differs only as regards level; in this case too the trichlorobiphenyl homolog congeners are an exception, showing low values of the correlation coefficients (e.g., $r_{PCB31/28\text{-}PCB52}= 0.838$).
The values of the "dissolved" and "particulate" concentration of PCBs found in a sample of water of the Canale della Scomenzera are reported in Tab. 2. The two fractions show similar concentration levels, higher than that found in Mediterranean Sea samples[3].

References

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